

Supporting Information

A rapid SERS method for label-free bacteria detection using polyethylenimine-modified Au-coated magnetic microspheres and Au@Ag nanoparticles

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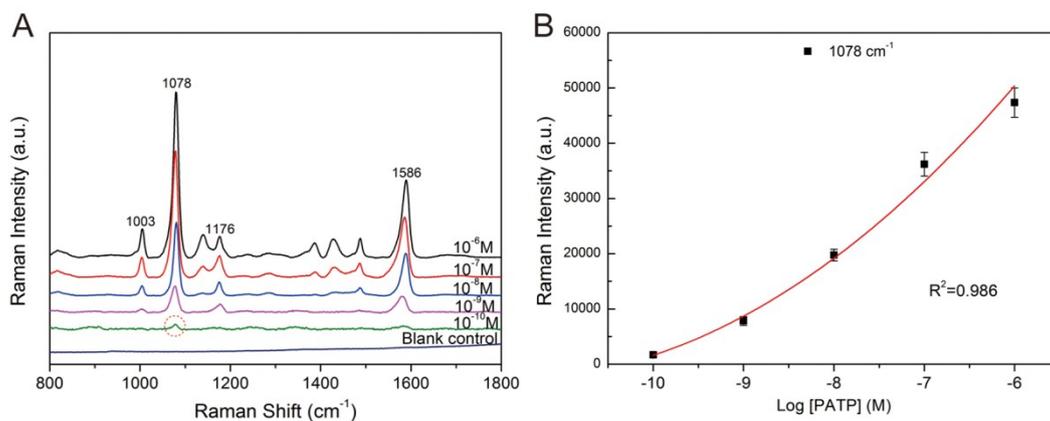


Fig. S1 (A) The SERS spectra of PATP measured with different concentrations on the Fe_3O_4 @Au microspheres. (B) Calibration curve for PATP at a concentration range of 10^{-10} to 10^{-6} M obtained by using SERS intensity at 1078 cm^{-1} . The error bars represent the standard deviations from 5 measurements.

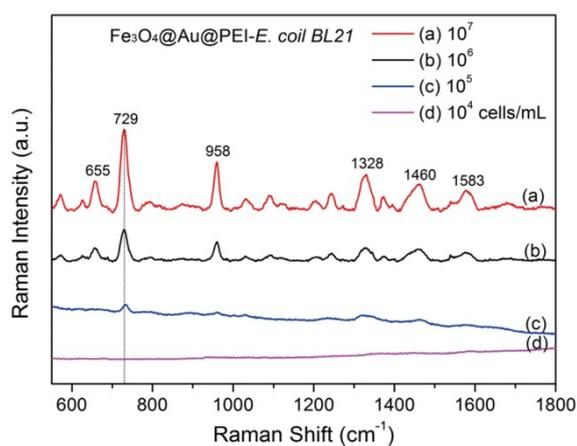


Fig. S2 SERS spectra of different concentrations of *E. coli* BL21 obtained with the $\text{Fe}_3\text{O}_4@Au@PEI$ microspheres as SERS substrates.

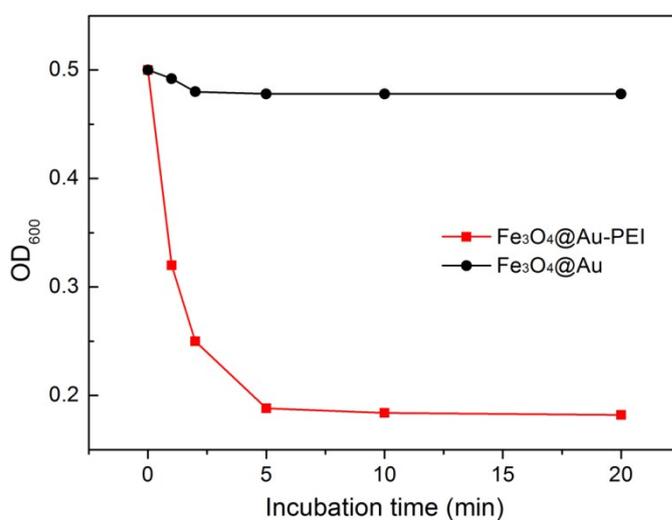


Fig. S3 Capture kinetics of the $\text{Fe}_3\text{O}_4@Au@PEI$ microspheres for *E. coli* BL21 at a regular shaking incubation of 250 rpm. The original concentrations of the bacteria in PBS (10 mM, pH 7.4) have an OD_{600} of 0.5.

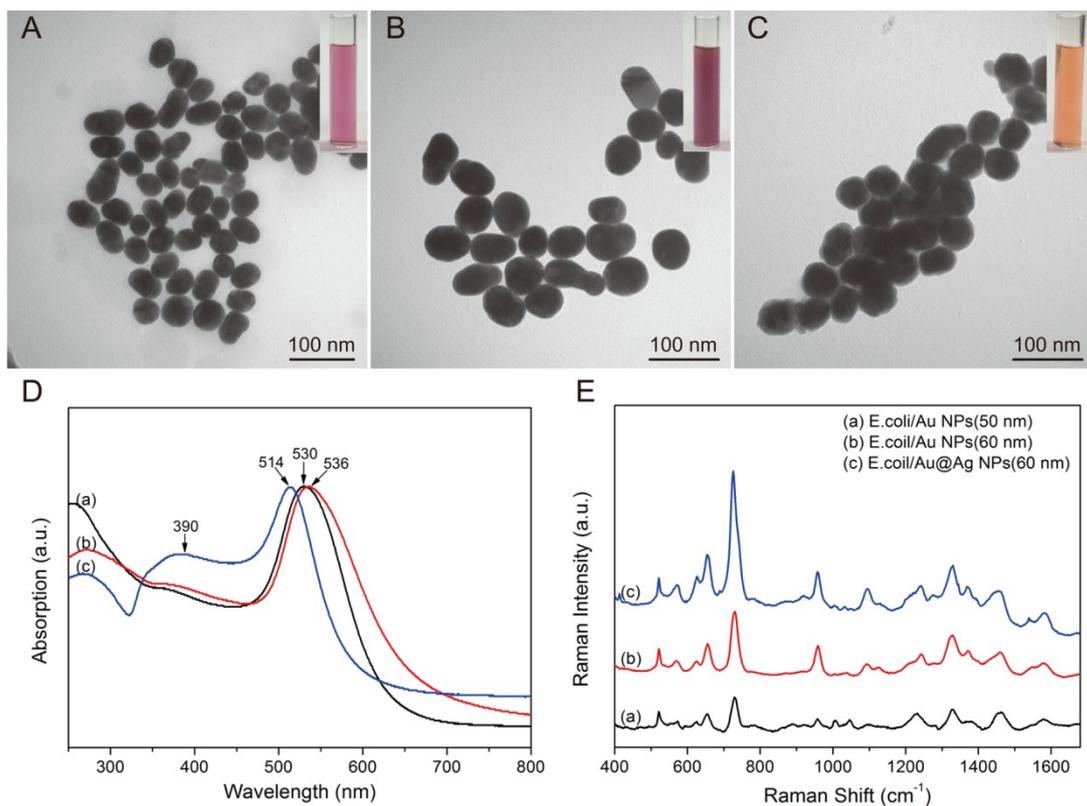


Fig. S4 TEM images of the synthesized enhanced nanoparticles: (A) 50 nm Au NPs, (B) 60 nm Au NRs, and (C) 60 nm Au@Ag NPs. The insets are the corresponding optical images. (D) UV-visible spectra of the synthesized enhanced nanoparticles. (E) Raman intensity of *E. coli* adsorbed on the three enhanced nanoparticles under the same conditions.

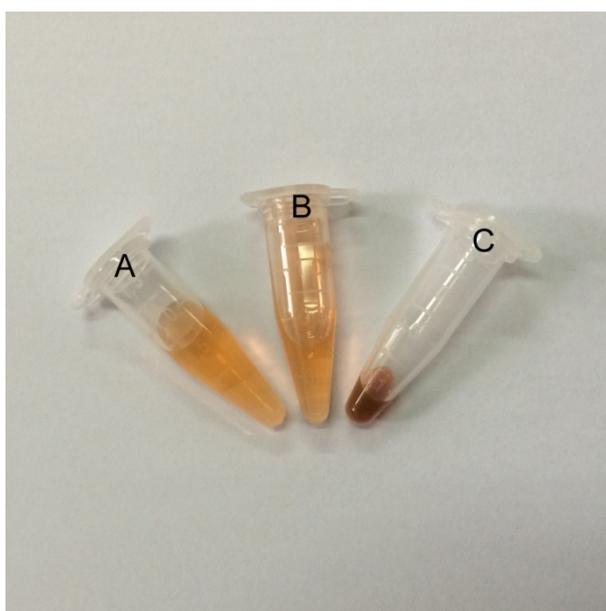


Fig. S5 True color photos of (A) Au@Ag NPs in aqueous solution, (B) Au@Ag NPs in ethanol, and (C) the concentrated Au@Ag NPs in ethanol.

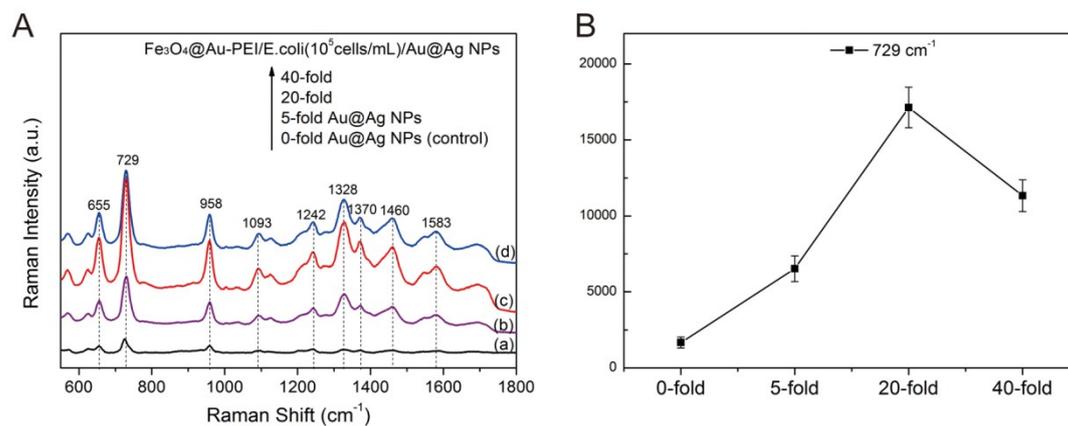


Fig. S6 Effect of the Au@Ag NPs concentrations in the CEE three-step method for bacteria *E. coli* detection. (A) SERS spectra of Au@Ag NPs by increasing their concentration from 0-fold to 40-fold. (B) Plot of 729 cm^{-1} band intensities versus the particle concentration of Au@Ag NPs from 0-fold to 40-fold. The error bars represent the standard deviation from five measurements.

Raman Shift (cm-1)	Assignments
563	carbohydrates
624	aromatic ring skeletal
655	$\delta(\text{COO}^-)$
729	adenine, glycosidic ring mode
958	$\nu(\text{CN})$
1093	amide III, adenine, polyadenine, DNA
1250-1310	amide III
1268	$\delta(\text{CH}_2)$ amide III
1328	$\nu(\text{NH}_2)$ adenine, polyadenine, DNA
1310-1440	$\nu(\text{COO}^-)$ symmetric
1370	$\nu(\text{COO}^-)$ and $\delta(\text{C-H})$ proteins
1440-1460	$\delta(\text{CH}_2)$ saturated lipids
1540-1645	amide II, $\nu(\text{CN})$, $\gamma(\text{NH})$
1640-1680	amide I

Table. S1 Raman peaks of *E. coli* BL21 and corresponding assignments.

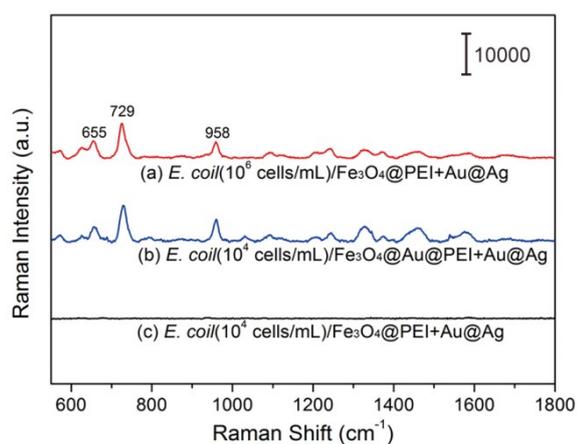


Fig. S7 SERS spectra of *E. coli BL21* in different systems: (a) *E. coli BL21* (10^6 cells/mL) obtained with the $\text{Fe}_3\text{O}_4@PEI$ microspheres and $Au@Ag$ NPs, (b) *E. coli BL21* (10^4 cells/mL) obtained with the $\text{Fe}_3\text{O}_4@Au@PEI$ microspheres and $Au@Ag$ NPs, and (c) *E. coli BL21* (10^4 cells/mL) obtained with the $\text{Fe}_3\text{O}_4@PEI$ microspheres and $Au@Ag$ NPs. All the Raman spectra were shifted for clarity.

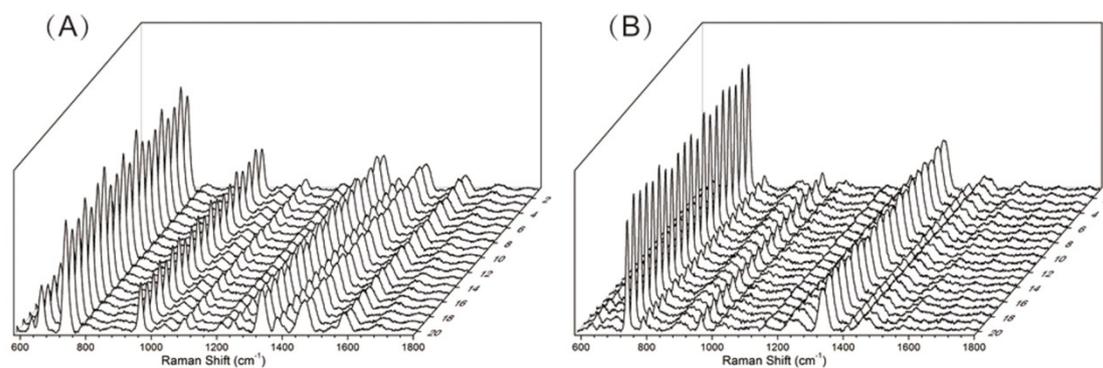


Fig. S8 SERS spectra collected from 20 randomly selected spots on the (A) $\text{Fe}_3\text{O}_4@Au@PEI$ -*E. coli*/ $Au@Ag$ complexes and (B) $\text{Fe}_3\text{O}_4@Au@PEI$ -*S. aureus*/ $Au@Ag$ complexes substrates.